Nucleation, Growth and Properties of sp³ Carbon Films Prepared by Direct C⁻ Ion Beam Deposition

Seong I. Kim

SKION Corporation, 612 River St. PO Box 3367, Hoboken, NJ 07030

Direct metal ion beam deposition is considered to be a whole new thin film deposition technique. Unlike other conventional thin film deposition processes, the individual deposition particles carry its own ion beam energies which are directly coupled for the formation of thin films Due to the nature of ion beams, the energies can be controlled precisely and eventually can be tuned for optimizing the process. SKION's negative C⁻ ion beam source is used to investigate the initial nucleation mechanism and growth. Strong C ion beam energy dependence has been observed. Complete phase control of sp³ and sp², control of the C/SiC/Si interface layer, control of crystalline and amorphous mode growth, and optimization of the physical properties for corresponding applications can be achieved.

Key words : Diamond, Ion beam deposition, Direct metal ion beam deposition, DLC, Amorphous diamond, Nucleation

I. Introduction

For the formation of diamond or DLC thin films, there are two major established technical approaches which are: Chemical Vapor Deposition (CVD) process-with the aid of atomic hydrogen, diamond phases are synthesized by chemical reaction of hydro carbon gases at relatively high temperatures (600~900C).[1] Physical Vapor Deposition (PVD) process-direct deposition of carbon particles at a low substrate temperature. Numerous studies such as nucleation, growth, and hydrogen effect etc. have been made in CVD process. However, relatively weak studies have been established in PVD process. One of the commonly understood facts in PVD process such as sputtering, laser ablation, arc etc. is that the incident energy of the carbon particle is the key factor which determines the phase of the DLC films [2-4] Unfortunately, there are no convenient experimental tools to change one of the most important variables=incident energy of carbon particle. SKION has introduced a novel negative metal ion beam source which is capable of producing various metal ion beams including carbon. SKION's ion source exhibits superior advantages such as compactness, low energy spread (± 10% at ion beam energy less than 100 eV), no particulates and solid state. Due to SKION's state-of-the-art solid state ion beam technology, one is able to investigate the nucleation and growth while maintaining Ultra Higy Vacuum (UHV < 10⁻⁹ Torr) environment. In this work, real time LEED and AES analysis have been performed to investigate the C ion beam energy dependence on initial nucleation mode.

II. Experimental procedure

SKION's negative metal ion beam source (NMIBSCS 02) is attached to the UHV surface analysis system equipped with AES, LEED, photo-electron threshold measurement, and Ar⁺ sputter ion gun. The background pressure is mid 10⁻¹¹ Torr and the pressure was maintained below 5×10^{-9} Torr while operating the C⁻ ion source. In order to investigate the initial growth stage, negative C⁻ ion beam current density at Si surface was controlled to about 1.0 µA/cm² which corresponds to he deposition rate of about 0.01 atomic layer/sec. The clean surface was obtained by Ar⁺ ion gun sputtering (3.5 keV and 10 µA) followed by thermal annealing (1000C for 10 min). A four grid reverse view Princeton Research Instrument (PRI) LEED optics and a Physical Electronics cylindrical mirror analyzer (CMA) with a coaxial electron gun are used.

III. Nucleation

The initial nucleation stages of carbon films have been investigated at C⁻ ion beam energies of 25, 50, 100, 125, and 150 eV. No external heating or cooling was made to the substrate during ion beam deposition. Fig. 1 shows the evolution of the carbon and silicon Auger line shapes as a function of C⁻ ion dose at C⁻ ion beam energy of 150 eV. For the initial low carbon dose up to 10¹⁶ ions/cm², the Auger line shape indicated that carbon grows in the SiC phase. The transition from SiC phase to sp³ carbon is found at around 5×10^{16} dose which corresponds to about 10 monolayers. Fig. 2 shows the cross section TEM
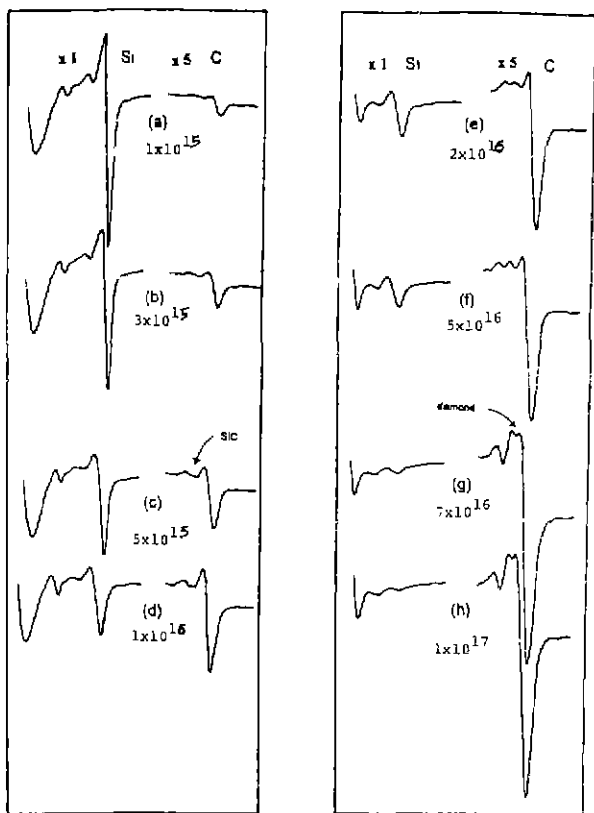
micrograph on the C/SiC/Si interface. Heteroepitaxial growth of diamond on Si has been observed. The interfacial SiC layers were grown in between Si(100) and Diamond (100) layers. Fig. 3 shows the LEED surface evolution from clean p(2×2) structure to p(1×1) structure for 3 atomic layers deposition. This result indicates the surface reconstruction to a SiC phase.
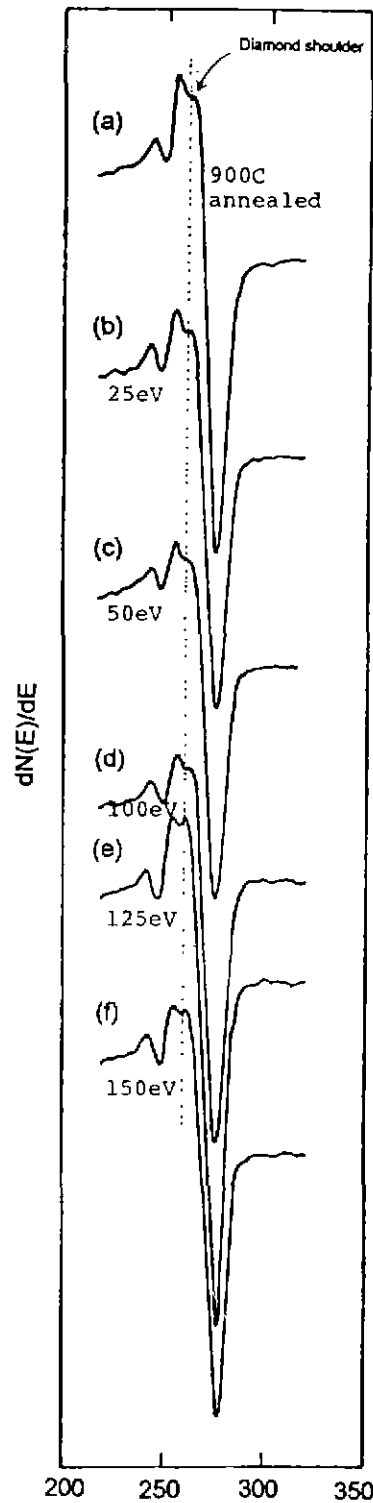

Fig. 1. Evolution of C and Si AES line spectra as a function of C ion dose at C⁻ ion beam energy of 150 eV.
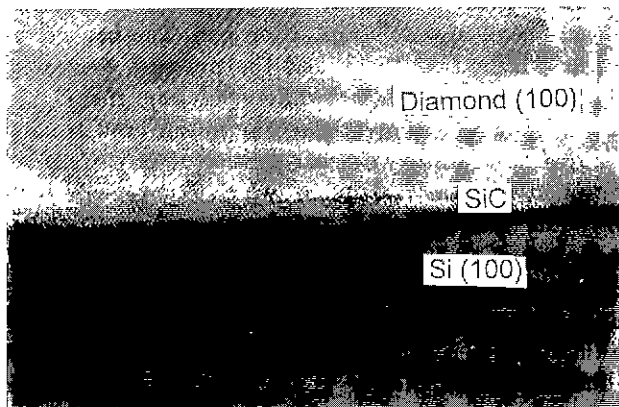
Fig. 2. Cross section TEM micrograh shows the diamond (100)/SiC/Si(100) interface.
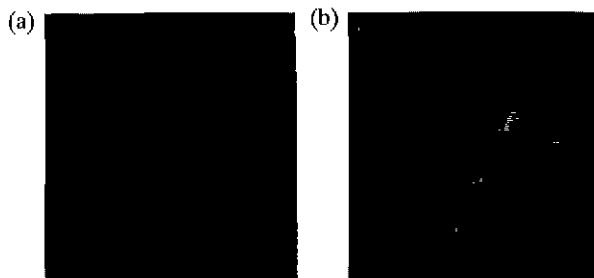
Fig. 3. LEED patterns of surface evolution by C ion beam deposition at 50 eV. (a) clean Si(100) surface and (b) 3ML of C⁻ ion beam deposition.

Fig. 4. AES C^{KLL} spectra for various C ion beam energies.

IV. Growth

The incident carbon particle energy dependence on the formation of sp²/sp³ phase was clearly revealed as shown in Fig. 4. The AES line structures on saturated dose (> 10^{17} ions/cm²) sample indicate that graphitic formation (sp² phase) was observed for samples produced at ion beam energy below 50 eV. At higher ion beam energy (> 100 eV), diamond (sp³ phase) structure is obtained. As shown in Fig. 2, heteroepitaxial growth of diamond films on Si(100) was obtained. The uniform nucleation and the lattice mismatch (> 50%) were two major obstacles for the heteroepitaxial diamond on Si. Utilizing energetic C⁻ ion beam, meta-stable interfacial SiC layer is formed. As shown in Fig. 5, the AES depth profile indicates that the

interfacial SiC layer has graded composition; i.e. Si rich at Si/SiC interface and sp³ C rich at C/SiC interface. Thus, SiC interface layer releases the stress as well as provides uniform nucleation of sp³ diamond.
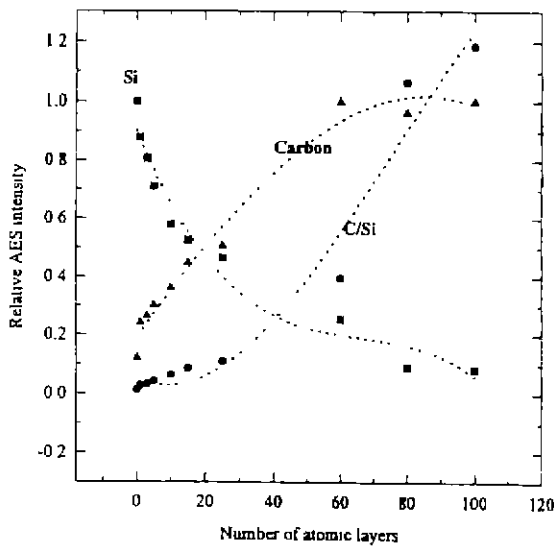

Fig. 5. AES depth profile of C/SiC/Si interface. The depth profile indicates that interfacial SiC layer has graded composition.
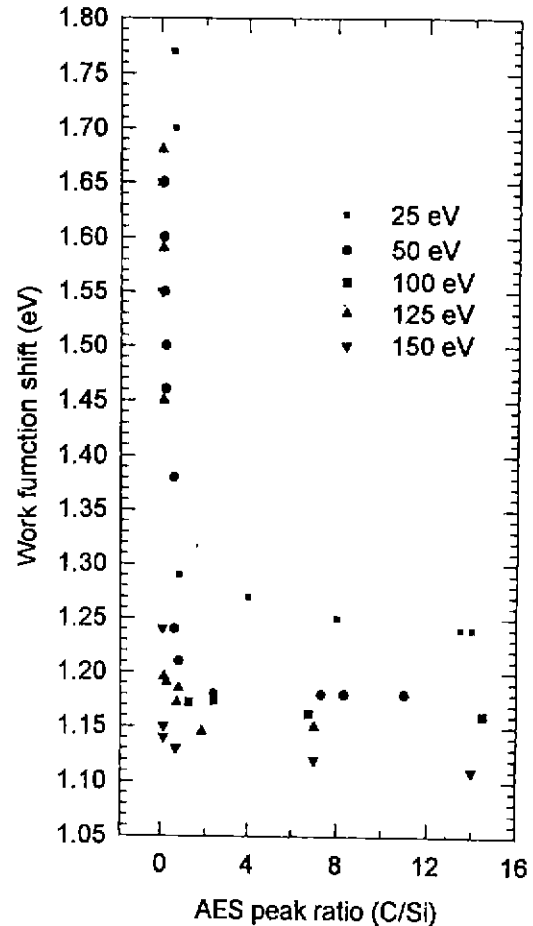

Fig. 7. Work function change of C-Cs compound films on Si as a function of C⁻ ion beam energy.
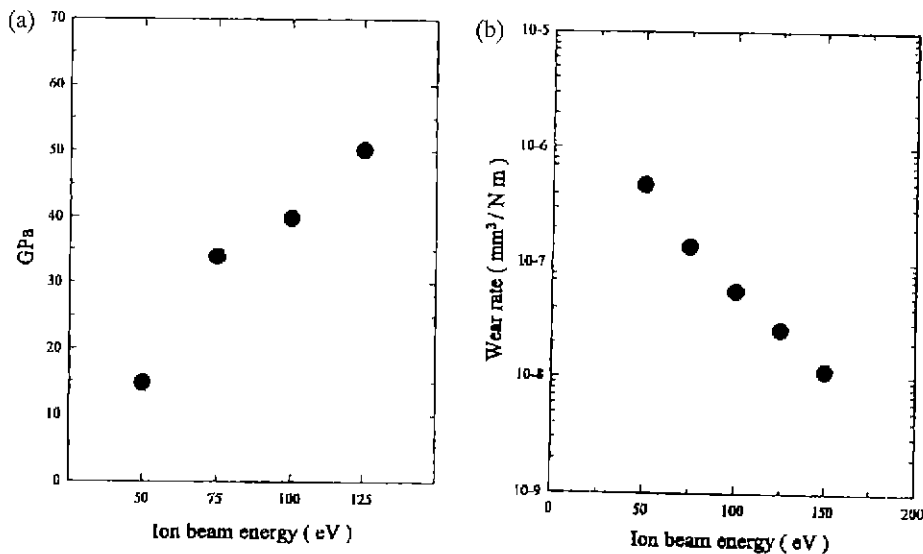

Fig. 6. Mechanical properties of C⁻ ion beam deposited films, (a) hardness measured by nanoindentation technique and (b) wear rate measured by ball-on-disk tribo-meter.

1. Mechanical properties

Fig. 6 shows the hardness of the films measured by nano indentation technique. The hardness strongly depends on the C$^-$ ion beam energy; the higher the C$^-$ ion beam energy, the higher the hardness of the films was obtained. At an energy more than 125 eV, 50~60 Gpa hardness is obtained. Wear rate is also measured using ball-on-disk tribo meter. Similar to the hardness, the wear rate is linearly reduced down to 10^{-8} mm^3/Nm at ion beam energy more that 125 eV. Atomic Force Microscopy (AFM) is used to measure the surface roughness. Ultra smooth surface (< 1 nm Ra) is measured for the samle produced at 100 eV of C$^-$ ion beam energy

2. Surface properties

Diamond is known to exhibit the Negative Electron Affinity (NEA) surface.[5,6] The work function of the film produced by codepostion of C$^-$ ion beam and Cs$^+$ ion bean is monitored by photo-electron threshold method. The flux ratio of C$^-$/Cs$^+$ is set to be 10. Fig. 7 shows the work function changes by C$^-$ & Cs$^+$ dose at different C$^-$ ion beam energies. The work function decreases with increasing C-Cs dose and eventually reaches a steady state value which represents the film property. As the C$^-$ ion beam energy increases, the work function is lowered.

V. Conclusion

The availability to control the incident C$^-$ ion beam energy with low energy spread makes it possible to study the carbon vapor deposition mechanism. As expected, the formation of sp^3 phase strongly depends on the incident energy. At 150 eV, physical properties close to natureal diamond have been obtained. Direct metal ion beam deposition process offers precise control of the ion beam energy which in turns optimized the properties of the films.

References

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